Indian J. Phys. **49**, 368-372 (1975)

X-ray study of photosensitive film on copper in aqueous solution of ferric chloride

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(*Received* 12 *November* 1974)

Photosensitive film is formed on electrolytic copper plate by treatment with aqueous solution of ferric chloride. The film is found to be of CuCl, by X-ray analysis. It is phototropic and photosensitive in nature. It gives photoprint and produces photocurrent when exposed to sunlight. The photocurrent increases to a maximum when the film is exposed in dry condition to sunlight; but if the film is exposed to sunlight after moistening with water, the photocurrent increases to maximum and then decreases and then becomes constant in about three minutes. The mechanism of change in polarity of the photocurrent is explained. The X-ray diffraction study of the film obtained shows the formation of (Cu_2O) cuprous oxide, as one of the products of primary photochemical reaction.

1. INTRODUCTION

Ferric chloride is an excellent etching agent for copper and has been extensively used in the preparation of printed circuits (Nekervis 1962, Saubestre 1959, Sharpe & Garn 1959). The product of action of ferric chloride on copper is CuCl which is insoluble in water and forms an adherent layer on the copper plate surface. Solid CuCl immersed in water exhibits photochromic properties as reported by number of workers (Hecht & Miller 1954, Wojtczak 1957, Singh 1922). But the photochromic property of CuCl as a pure product has been studied by these workers. The action of light on CuCl film on copper plate in presence of moisture has not been reported. Thin films have properties different from pure products. The base copper metal surface as well as photoadsorption of oxygen has catalytic effect on photochemical reaction with CuCl. In the present work the product of photochemical reaction with CuCl in presence of moisture and oxygen has been studied by X-ray diffraction study of the film in contact with the copper plate. The study shows that the primary photo chemical reactions produces (Cu_2O) cuprous oxide. Secondary products have not been investigated. The formation of Cu_2O is also supported by the study of reversal of photocurrent when CuCl film is exposed to light moistened with water.

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2. Experimental

A copper specimen of 99.8% Cu was used. Cleaned and polished accorrding to the method suggested by Champion (1952). The cleaned copper was immersed in 0.1*M* aqueous ferric chloride solution for 10 minutes at room temperatures. Then it was washed with distilled water and dried. This operation was carried out in the dark. The film on half the surface of the plate was scraped out completely. The film on the back side of the plate was also scraped out. The film surface and the copper surface were connected to a sensitive ballistic galvanometer by silver paint contact and exposed to sunlight in dry condition and the photocurrent was measured with time of exposure. The experiment was repeated by measuring the photocurrent after moistening the film with distilled water. For X-ray diffraction study the film was prepared chemically on the copper plate as described above and the film in contact with copper plate was used for X-ray diffraction study. The X-ray equipment used was a of Philips Inc. Holland type PW 1009 with extra stabilizer unit. A 800 watt water cooled Philips tube having a copper target was used as the X-ray tube. The X-ray beam was passed through a nickel filter to cut off the β-component. It emerged at an angle of 6° to the normal to the tube window. The copper plate having the film on its surface was put at the centre of the horizontal diffractometer disc. The disc was calibrated in degree (θ), each degree divided into four parts and had a diameter of 500 mm. The Geiger counter was enclosed in a cylindrical enclosure with a slit in front of it, and the counter could be rotated on the graduated scale about the specimen. The specimen was flat having an area of 6×3 sq. cm. and rotated at half the speed at which the Geiger counter was rorated, so that its surface remained tangential to the focussing circle. The Geiger counter was rotated by a synchronous motor at the speed of half a minute per degree. A screening plate with a slit of about 3 mm was placed in front of the counter to cut off stray radiation. The pulse of the Geiger counter was fed to a ratemeter through an amplifying circuit. A micrometer put in the ratemeter showed a diffraction whenever a Geiger counter passed across an X-ray line. Thus the position of the X-ray line could be located and read on the diffraction scale. The scale of the microammeter was directly calibrated in counts per second, and could be read upto maximum 30,000 per second. The recorder was run 1200 mm per minute. The wave length of X-ray used was 1.5405 A.U. The X-ray diffraction spectrum of the film was taken.

Next a polished copper plate 6×3 sq.cm. was mounted on the diffractometer disc and X-ray diffraction spectrum for copper was recorded.

Finally cuprous oxide (B.D.H. quality) was pressed on a glass slide. This was mounted on the diffractometer disc and the X-ray diffraction spectrum for cuprous oxide was recorded.

3. Discussion

Ferric chloride reacts with copper giving CuCl which remains adherent on the copper plate.

$$2FeCl_3 + Cu \rightarrow CuCl_2 + 2FeCl_2$$

$$CuCl_2 + Cu \rightarrow 2CuCl.$$

Pourbaix (1967) associated a depression of potential of copper brought about by illumination with the presence of cuprous chloride on its surface. Lucey (1967) indicated that illumination of copper produced a more negative potential if the metal was covered by cuprous chloride film and a more positive potential when it was covered by a cuprous oxide film. They have utilized these observations to explain pitting corrosion of copper pipes. CuCl is photosensitive and when sunlight falls on it produces a photocurrent which changes its polarity with time (Franceo & Patel 1973). It is also photosensitive and gives a photoprint. When sunlight falls on CuCl film formed on copper exposed in dry condition, the photocurrent increases to maximum but on moistening the film with distilled water the photo current increases to maximum and then decreases or reverses and then in about three minutes becomes constant. The reversal if photocurrent has been attributed to photosolvation followed by photooxidation due to presence of photoadsorbed oxygen. CuCl is an n type semiconductor. It is photosensitive and produces photocurrent

$$CuCl + nH_2O \xrightarrow{h\nu} \underset{\text{(complex)}}{CuCl.....H_2O}$$

$$\underset{\text{(complex) photoadsorbed}}{CuCl.....H_2O} + O_2 \rightarrow Cu_2O + HCl + \text{other products}$$

Cu_2O is formed as a result of photoreaction given above. As Cu_2O is a p-type semiconductor, the presence of CuCl and Cu_2O forms an n–p semiconductor junction which explains the leveling of photocurrent in three minutes. The formation of Cu_2O was proved by X-ray diffraction study. The X-ray diffraction study of the film shows peaks for Cu_2O, Cu and CuCl. All have cubic lattice. The values for a for Cu, Cu_2O and CuCl lattice are 3.608 A.U., 4.26 A.U. and 5.407 A.U. respectively (Hodgman *et al* 1959). The diffraction angle (θ) for peaks were theoretically calculated for different h, k, l values using the equation

$$\frac{\lambda}{2\sin\theta} = \frac{a}{(h^2+k^2+l^2)^{\frac{1}{2}}}$$

and these values were compared with those obtained in the X-ray diffraction spectrum. Figure 1 is the X-ray diffraction spectrum for the film obtained on copper plate. It shows peaks for cuprous-chloride at diffraction angles 14°17′,

23°45′ and 28°11′ and also peaks for cuprous oxide (Cu_2O) at diffraction angles 18°15′ and 30°45′ and peaks for copper (due to the copper base below the film) at diffraction angle 21°41′ and 37°8′, figures 2 and 3 are X-ray diffraction spectrums for copper and (Cu_2O) cuprous oxide taken to confirm the peaks obtained for Cu and Cu_2O in figure 1 for the film product.

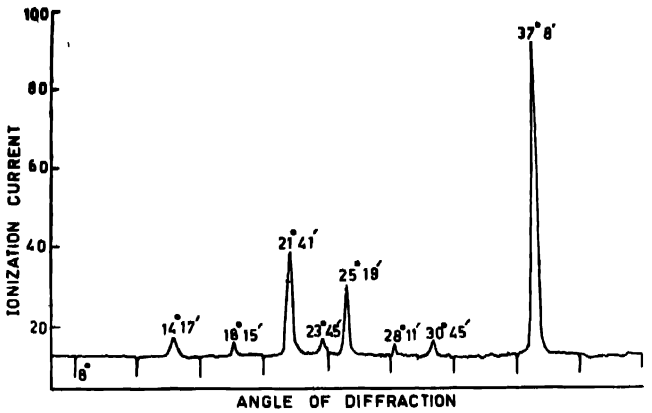

Fig. 1. X-ray diffraction spectrum of CuCl film on copper plate, after exposure to sunlight in presence of moisture.

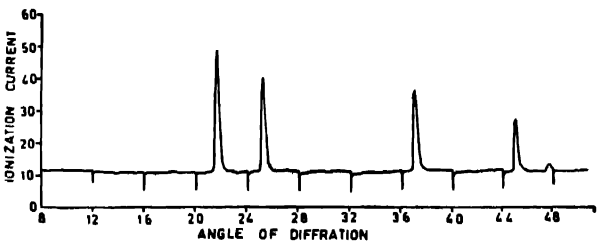

Fig. 2. X-ray diffraction spectrum of copper.

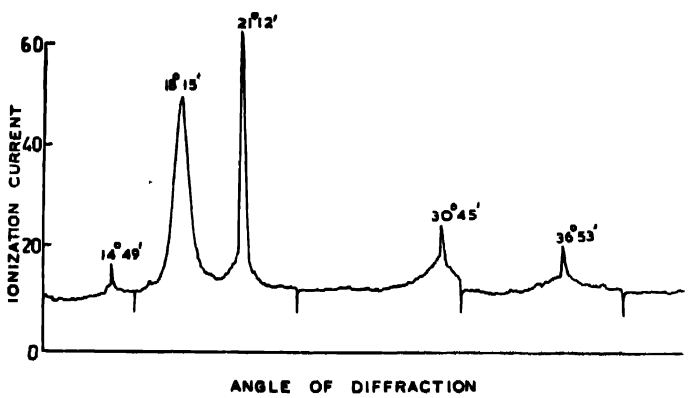

Fig. 3. X-ray diffraction spectrum of cuprous oxide.

4. Conclusions

The formation of photoprint on the CuCl film obtained on copper may be due to photochemical reactions between CuCl, water and photoadsorbed oxygen in presence of sunlight. The primary photochemical reaction gives rise to formation of cuprous oxide (Cu_2O). The photo current increases to maximum, reverses and then levels off within three minutes. This levelling of photocurrent may be due to presence of CuCl an *n*-type semiconductor and Cu_2O a *p* type semiconductor forming *n–p*- junction. The X-ray diffraction study confirms the formation of cuprous oxide (Cu_2O).

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